Dynamics of ion-phosphate lattice of DNA in left-handed double helix form

S.M. Perepelytsya, S.N. Volkov
Bogolyubov Institute for Theoretical Physics, NAS of Ukraine,
14-b Metrolohichna St., Kiev, 03680, Ukraine

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Abstract

The conformational vibrations of Z-DNA with counterions are studied in framework of phenomenological model developed. The structure of left-handed double helix with counterions neutralizing the negatively charged phosphate groups of DNA is considered as the ion-phosphate lattice. The frequencies and Raman intensities for the modes of Z-DNA with Na^+ and Mg^{2+} ions are calculated, and the low-frequency Raman spectra are built. At the spectra range about the frequency 150 cm^{-1} new mode of ion-phosphate vibrations is found, which characterizes the vibrations of Mg^{2+} counterions. The results of our calculations show that the intensities of Z-DNA modes are sensitive to the concentration of magnesium counterions. The obtained results describe well the experimental Raman spectra of Z-DNA.

1 Introduction

DNA is macromolecule with the double helix structure which may adopt different forms as a response to changes of environmental conditions [1–5]. Under the natural conditions the double helix is right-handed due to the stabilization by metal ions (counterions) that neutralize the negatively charged phosphate groups of the macromolecule backbone. Increasing the concentration of counterions the double helix may take the left-handed conformation with zigzag like backbone (Z-form), which is significant in many biological processes [6]. The study of counterion influence on the structure and dynamics of the left-handed form of the double helix is important for the understanding the mechanisms of DNA biological functioning.

The counterions of different type may be localized in different manner with respect to the double helix phosphate groups. The experimental data for solid samples of DNA show that monovalent counterions are usually localized near the oxygen atoms of the phosphate groups from the outside of the macromolecule [7, 8], while the counterions of higher charge may neutralize the phosphate groups of different DNA strands or bind to the nucleic bases [9]. In the solution the counterions do not have defined positions, and they form a shell near DNA surface [10–13]. In experiment this shell is observed as a cloud around the double helix [14–17]. The molecular dynamics simulations of DNA counterions in water solution show that the residence time of counterions near the phosphate group of DNA backbone is about 1 ns [18, 19]. In this time scale the counterions may form a regular structure around the double

helix. Such structure of counterions and DNA phosphate groups may be considered as a lattice of ionic type (ion-phosphate lattice).

The DNA ion-phosphate lattice is expected to have properties of ionic crystals, therefore it should be characterized by counterion vibrations with respect to the phosphate groups (ion-phosphate vibrations). The ion-phosphate vibrations must be coupled with the internal vibrations of the double helix, since the dynamics of the ion-phosphate lattice is the part of DNA conformational dynamics. The determination of DNA ion-phosphate modes is of paramount importance for the understanding of counterion influence on the structure and dynamics of DNA double helix.

The DNA ion-phosphate vibrations may be observed in the low-frequency spectra ($10 \div 200$ cm^{-1}) where the ion vibrations in ionic crystals and electrolyte solution are prominent [20,21]. In this spectra range the modes of DNA conformational vibrations are also observed [22–25], which are characterized by the displacements of the atomic groups in the nucleotide pairs (phosphates, nucleosides and nucleic bases) from their equilibrium positions [26–29]. The conformational vibrations of the right-handed forms of the double helix are described well within the framework of the phenomenological approach [26–29]. In our previous works [30–35] this approach has been extended for the case of vibrations of the monovalent couterions with respect to the phosphate groups, and the ion-phosphate vibrations are determined for the right-handed double helix with Na^+, K^+, Rb^+, and Cs^+ counterions. The results have been showed that the frequencies of ion-phosphate vibrations decrease as counterion mass increases from 180 to 90 cm^{-1}. The character of DNA conformational vibrations is found to be very sensitive to the counterion type and localization with respect to the double helix atomic groups [34,35].

In case of Z-DNA the character of conformational vibrations may be essentially different because the structure of the left-handed double helix has the unique features. The phosphate groups of the left-handed double helix form a backbone with zigzag shape and the nearest base pairs have different overlapping. Therefore, the nucleotide pairs form the dimers which are the elementary units of Z-DNA [1]. The overlapping of the base pairs inside dimer is stronger than between dimers. In the same time, the dimeric structure of Z-DNA is also stabilized by counterions (usually Mg^{2+}) that may be localized between phosphate groups of different strands of the double helix. The formation of dimers by nucleotide pairs and the localization of counterions in the DNA minor grove may be essential for the low-frequency modes of Z-DNA. The experimental data show that in the low-frequency spectra of Z-DNA new modes near 150 and 42 cm^{-1} are observed [36]. The origin of these modes is not determined yet. To describe the low-frequency spectra of Z-DNA the approach [30–35] should be extended considering the features of the structure of zigzag like form of the double helix and possible cases of counterion localization with respect to the phosphate groups.

The goal of the present work is to find the modes of optic type for Z-DNA with counterions and to describe the conformational dynamics of the left-handed double helix. To solve this problem in section 2 the approach for the description of dynamics of DNA ion-phosphate lattice [30–35] is extended for the case of Z-DNA. In section 3 the frequencies and the Raman intensities of the modes of DNA conformational vibrations are calculated and the low-frequency spectrum of Z-DNA is built. Using the calculated spectrum the origin of new modes of Z-DNA observed in the experimental spectra is determined.

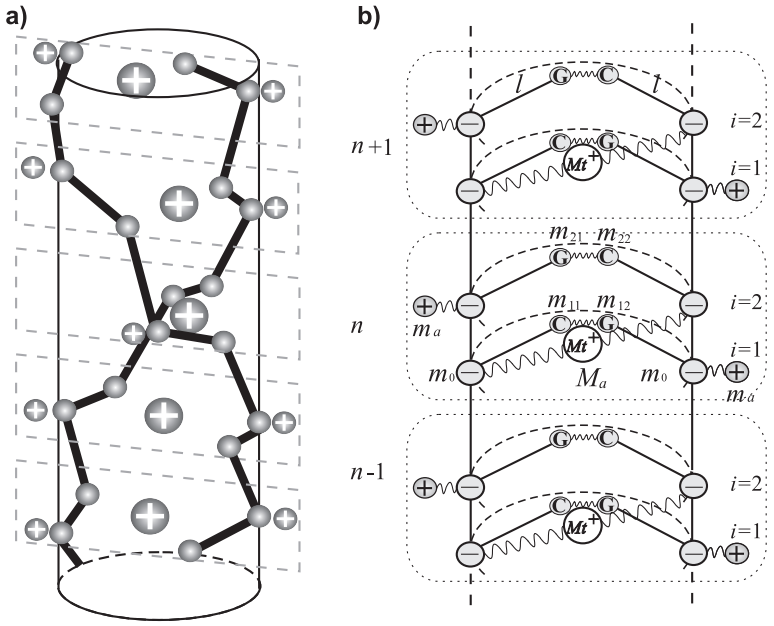

Figure 1: Ion-phosphate lattices of Z-DNA. (a) Zigzag-like shape of Z-DNA backbone. (b) Model for conformational vibrations of the left-handed double helix with counterions. The monomer links of the model consisted of two nucleotide pairs (dimers) are showed by dotted frames.

2 Model for conformational vibrations of ion-phosphate lattice of Z-DNA

To describe the conformational dynamics of DNA ion-phosphate lattice the typical cases of counterion localization with respect to the phosphate groups should be considered. Usually the monovalent counterions are localized from the outside of the double helix, where one monovalent counterion neutralizes one phosphate group (single-stranded position of counterion). In the same time, due to the zigzag like shape of the backbone of Z-DNA (Fig. 1a), the distance between phosphate groups of different strands is rather short that makes possible the localization of counterions in the minor grove of the left-handed double helix between phosphates of different strands (cross-stranded position of counterion). The cross-stranded position is more favorable for bivalent counterions (Fig. 1a).

To describe the conformational vibrations of DNA double helix the phenomenological approach [26–28] is used. In framework of this approach the phosphate groups (PO_4+$C_{5'}$) and nuclosides are modelled as masses m_0 and m, respectively. The nucleosides rotate as the physical pendulums with respect to the phosphate groups in plane of nucleotide pair. The physical pendulums are characterized by reduced length l. The nucleosides of different chains are paired by H-bonds (Fig. 1b). The motions of structural elements of the monomer link are considered in the plane orthogonal to the helical axis (transverse vibrations). The longitudinal vibrations of the macromolecule atomic groups have much higher frequencies and are beyond the scope of this work.

According to the dimeric structure of the zigzag lake double helix the monomer link of the model of Z-DNA consists of two nucleotide pairs. The nucleosides in dimer usually have

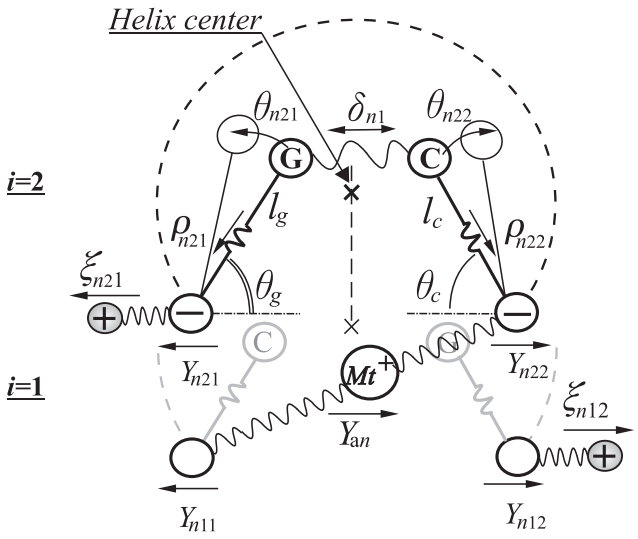

Figure 2: Monomer link of the left-handed double helixes (dimer of nucleotide pairs). l is reduced length of pendulum-nucleoside; θ_0 is equilibrium angle; m, m_0, and m_a are masses of nucleosides, phosphate groups, and counterions, respectively; X, Y, θ, ρ, and ξ are vibrational coordinates of the model (see text). The arrows indicate positive directions of displacements.

alternated sequence of guanine (G) and cytosine (C) nucleic bases [1]. The displacements of nucleosides and phosphate groups in DNA monomer link are described by coordinate Y. The coordinate θ describes the deviations of pendulum-nucleosides from their equilibrium position (angle θ_0) in the plane of complementary DNA pair. The vibrations of deoxyribose and base with respect to each other, inside the nucleoside (intranucleoside mobility), are described by changes of pendulum lengths ρ. The vibrations of counterion in single-stranded positions are described by coordinate ξ. For description of vibrations of a counterion in cross-stranded positions the coordinate Y_a is used. The vibrational coordinates of the model and the positive directions of displacements are showed on Figure 2.

Within the framework of introduced model of the dynamics of DNA ion-phosphate lattice the energy of vibrations of structural elements of the double helix may be written as follows:

$$E = \sum_n \left(K_n + U_n + U_{n,n-1} \right), \tag{1}$$

where K_n and U_n are the kinetic and potential energies of the monomer link n of DNA ion-phosphate lattice, $U_{n,n-1}$ is the potential energy of interaction along the chain. The kinetic energy of the monomer link may be written as follows:

$$K_n = K_{0n} + K_{an}, \tag{2}$$

where K_{0n} and K_{an} are the energies of vibrations of structure elements in nucleotide pairs of n-th dimer and counterions, respectively. The potential energy of displacements of the masses in monomer link may be written as follows:

$$U_n = U_{0n} + U_{an}, \tag{3}$$

where U_{0n} and U_{an} are the energy of vibrations of the masses in nucleotide pairs of dimer and the energy of vibrations counterions, respectively.

The expressions for K_{0n} and U_{0n} for Z-DNA may be written in the following form:

$$K_{0n} = \frac{1}{2}\sum_{i}^{2}\sum_{j}^{2}[M_{ij}\dot{Y}_{nij}^2 + m_{ij}(\dot{\rho}_{nij}^2 + l_{ij}^2\dot{\theta}_{nij} + 2l_{ij}^s\dot{\theta}_{nij}\dot{Y}_{nij} + 2b_{ij}\dot{\rho}_{nij}\dot{Y}_{nij})], \tag{4}$$

$$U_{0n} = \frac{1}{2}\sum_{i}^{2}[\alpha\delta_{ni}^2 + \sum_{j}^{2}(\sigma_{ij}\rho_{nij}^2 + \beta_{ij}{\theta_{nij}}^2)] + \frac{1}{2}\sum_{j}^{2}[g_\theta(\theta_{n1j} - \theta_{n2j})^2 + g_\rho(\rho_{n1j} - \rho_{n2j})^2 + \tag{5}$$
$$+ g_y(Y_{n1j} - Y_{n2j})^2],$$

where $l_{ij}^s = l_{ij}a_{ij}$; $a_{ij} = \sin\theta_{0ij}$; $b_{ij} = \cos\theta_{0ij}$; n enumerates dimers of macromolecule; $i = 1, 2$ enumerates the nucleotide pairs in these dimers; $j = 1, 2$ enumerates the chain of the double helix; α, σ_{ij}, and β_{ij} are the force constants describing H-bond stretching in base pairs, intranucleoside mobility, and rotation of nucleosides with respect to the backbone chain in base-pair plane, respectively; g_θ, g_ρ, and g_y are the force constants describing the interaction of nucleic bases and the interaction between phosphate groups of different nucleotide pairs in dimers. The variable δ_{ni} describes stretching of H-bonds in the base pairs (Fig. 2). In the present work it is determined analogically to [27, 28]: $\delta_{ni} \approx l_{si1}\theta_{ni1} + l_{si2}\theta_{ni2} + Y_{ni1} + Y_{ni2} + b_{i1}\rho_{ni1} + b_{i2}\rho_{ni2}$.

The kinetic and potential energies of counterion vibrations in the ion-phosphate lattice of Z-DNA may be written as follows:

$$K_{an} = \frac{m_a}{2}[(\dot{Y}_{n21} + \dot{\xi}_{n21})^2 + (\dot{Y}_{n12} + \dot{\xi}_{n12})^2] + \frac{M_a}{2}\dot{Y}_{an}^2, \tag{6}$$

$$U_{an} = \frac{\gamma}{2}(\xi_{n21}^2 + \xi_{n12}^2) + \frac{\gamma_a}{2}\left[(Y_{an} - Y_{n22})^2 + (Y_{an} + Y_{n11})^2\right], \tag{7}$$

where γ and γ_a are the force constants for the counterions in single-stranded and cross-stranded positions, respectively; m_a and M_a are the masses of counterions in single-stranded and cross-stranded positions, respectively. In equation (6) and (7) the first terms describe the kinetic and potential energy of vibrations of counterions in single-stranded positions, while the last terms describe the the kinetic and potential energy of vibrations of counterions in cross-stranded positions.

To describe the low-frequency Raman spectra of Z-DNA we intent to find the optic type phonons, which are observed in the experimental spectra from 10 to 200 cm^{-1}. Therefore, we will consider the modes characterizing the vibrations of DNA atomic groups inside the Z-DNA monomers (dimers of nucleotide pairs) which are prominent in the considered spectra range. The vibrations of the pair dimers with respect to each other by our estimations occur with essentially lower frequencies (< 5 cm^{-1}). Since only the long-range optic vibrations are observed in the low-frequency Raman spectra we will consider the limited long-wave ($\bar{k} \to 0$) vibrational modes of the ion-phosphate lattice in Z-DNA. From the point of the theory of the lattice vibrations such approximation is the same as the neglecting interaction along the chain [37]. So, in the following consideration we neglect the interaction term: $U_{n,n-1} \approx 0$. Within the framework of this approximation the equations of motions may be written as follows:

$$\frac{d}{dt}\frac{\partial K_{0n}}{\partial \dot{q}_n} + \frac{d}{dt}\frac{\partial K_{an}}{\partial \dot{q}_n} - \frac{\partial U_{0n}}{\partial q_n} - \frac{\partial U_{an}}{\partial q_n} = 0, \tag{8}$$

where q_n denotes some vibrational coordinate in the monomer link of model (Fig. 2). The equations of motion (8) in explicit form for the model coordinates of Z-DNA double helix are showed in Appendix.

To estimate the frequencies of Z-DNA conformational vibrations the force constants $\alpha = 85$ kcal/molÅ^2, $\beta = 40(46)$ kcal/mol, $\sigma = 43(22)$ kcal/molÅ^2 are used the same as in $B(A)$-DNA [26, 27]. The values of β and σ in case of the left-handed Z-DNA are different for G and C nucleosides, and they are taken the same as in A- and B-forms, respectively. The constants g_θ and g_ρ are equal to 20 kcal/mol, while the constant $g_y = 8$ kcal/molÅ^2, [26, 27]. The structure parameters of the model (l and θ_0) for Z-DNA are determined using the X-ray data (pdb code: 1dcg) [38].

The constants of ion-phosphate vibrations have been determined in our previous works [31, 35], by using the theory of ionic crystals. It has been showed that the constant of ion-phosphate vibrations depends mostly on dielectric constant of DNA ion-hydrate shell, the Madelung constant of the system describing the electrostatic interaction of the ion with all charges of the system, and parameters of the ion (Pauling radius of cation and oxygen atom). The dielectric constant has been determined considering the properties of the hydration shell of DNA with the counterions of different type. The Madelung constant has been calculated from the structure of the double helix. As the result the values of γ and γ_a constants have been calculated for the case of ion-phosphate lattice of DNA with alkali metal counterions in single-stranded position and for magnesium counterions in cross-stranded position. The magnesium counterions are considered with the hydration shell because the size of hydrated Mg^{2+} ion corresponds to the distances between phosphate groups of the left-handed double helix. The hydration shell of magnesium ion consists of 4 water molecules that are strongly bond with the ion [39]. Thus, the constants of ion-phosphate vibrations have the following values: $\gamma = 52$ kcal/mol Å^2 in case of Na^+ counterions [31], while in case of Mg^{2+} $\gamma_a = 62$ kcal/mol Å^2 [35]. Using such parameters the frequencies of Z-DNA conformational vibrations are estimated by the formulae (1) – (8).

3 The low-frequency Raman spectra of *Z*-DNA

According to the character of vibrations of structural elements in DNA nucleotide pairs the obtained modes may be classified as the modes of ion-phosphate vibrations (**Ion**), H-bond stretching modes (**H**), modes of intranucleoside vibrations (**S**), and modes of backbone vibrations (**B**). To characterize the influence of counterion mobility the frequencies of Z-DNA conformational vibrations for the dimers without Mg^{2+} counterions are also calculated. The frequency values for Z-DNA conformational vibrations are showed in the Table 1.

The calculations show that the frequencies of ion-phosphate vibrations depend on counterion position. In case of Na^+ counterions in single-stranded position there are two degenerated modes (ω_{Ion1} and ω_{Ion2}) with the frequencies at the top of DNA low-frequency spectra (near 180 cm^{-1}). These modes are characteristic for the both right- and left-handed double helix forms. The vibrations of hydrated Mg^{2+} ions in cross-stranded position (ω_{Ion3}) have essentially lower frequency that is due to the big size and big mass of hydrated Mg^{2+} ion ($M_a = 96$ a.u.m.). The vibrations of Mg^{2+} counterion in cross-stranded position do not influences the vibrations

Table 1: Frequencies of Z-DNA conformational vibrations (cm^{-1}). The results for two cases are showed: Z-DNA with Na^+ and Mg^{2+} counterions, and Z-DNA with Na^+ counterions only. The calculated frequencies are compared with the experimental data for Z-DNA [23, 36] and with the calculation data for B-DNA [31].

		Z-DNA				B-DNA
		Theory		Experiment*		Theory [31]
Mode		(Na^+, Mg^{2+})	(Na^+)	[36]	[23]	(Na^+)
Ion	ω_{Ion1}	180	180	–	–	181
	ω_{Ion2}	180	180	–	–	181
	ω_{Ion3}	152	–	153w	–	–
H	ω_{H1}	110	107	112s	116sh	110
	ω_{H2}	106	106	–	100	–
	ω_{H3}	96	68	–	–	–
	ω_{H4}	59	66	70	66	58
S	ω_{S1}	45	45	45vw	–	79
	ω_{S2}	44	41	–	–	–
	ω_{S3}	40	28	–	–	–
B	ω_{B1}	25	25	25	–	16
	ω_{B2}	20	20	–	–	14
	ω_{B3}	11	11	–	–	–
	ω_{B4}	11	11	–	–	–

* s – strong, sh – shoulder, w – weak, vw – very weak.

of Na^+ counterions outside of the double helix.

The H-bond stretching in nucleotide pairs of Z-DNA are characterized by 4 modes (ω_{H1}, ω_{H2}, ω_{H3}, and ω_{H4}), while in the case of the right-handed form of the double helix there are only two modes. Additional two modes of H-bond stretching ω_{H2} and ω_{H3} appear due to the formation of dimers of nucleotide pairs in Z-DNA structure. The modes ω_{H1} and ω_{H2} have practically the same frequency for B- and Z-DNA. The modes ω_{H3} and ω_{H4} of Z-DNA are sensitive to Mg^{2+} counterion in cross-stranded position.

In case of left-handed double helix there are 3 modes of intranucleoside vibrations ω_{S1}, ω_{S2}, and ω_{S3} with rather close frequency values (about 45 cm^{-1}). The modes of intranucleoside vibrations depend essentially on the double helix form. In case of B-DNA there is only one mode of intranucleoside vibrations ω_{S1}, which has essentially higher frequency than respective modes of Z-DNA. The mode ω_{S3} shifts to lower frequencies if there is no Mg^{2+} counterion in cross-stranded position.

The modes of backbone vibrations (ω_{B1}, ω_{B2}, ω_{B3}, and ω_{B4}) are the lowest in DNA low-frequency spectra. In case of the ion-phosphate lattice of Z-DNA there are two modes (ω_{B1}, ω_{B2}) near 25 cm^{-1} and two modes (ω_{B3}, ω_{B4}) with close frequency values (about 10 cm^{-1}). In case of the ion-phosphate lattice of B-DNA there are only two modes ω_{B1} and ω_{B2} with close frequency values. This difference of B- and Z-DNA spectra is the manifestation of the dimeric structure of the left-handed structure of DNA double helix.

To compare our calculations with the experimental spectra the Raman intensities are calculated using the approach developed in [34,35]. As the result the low-frequency Raman spectra

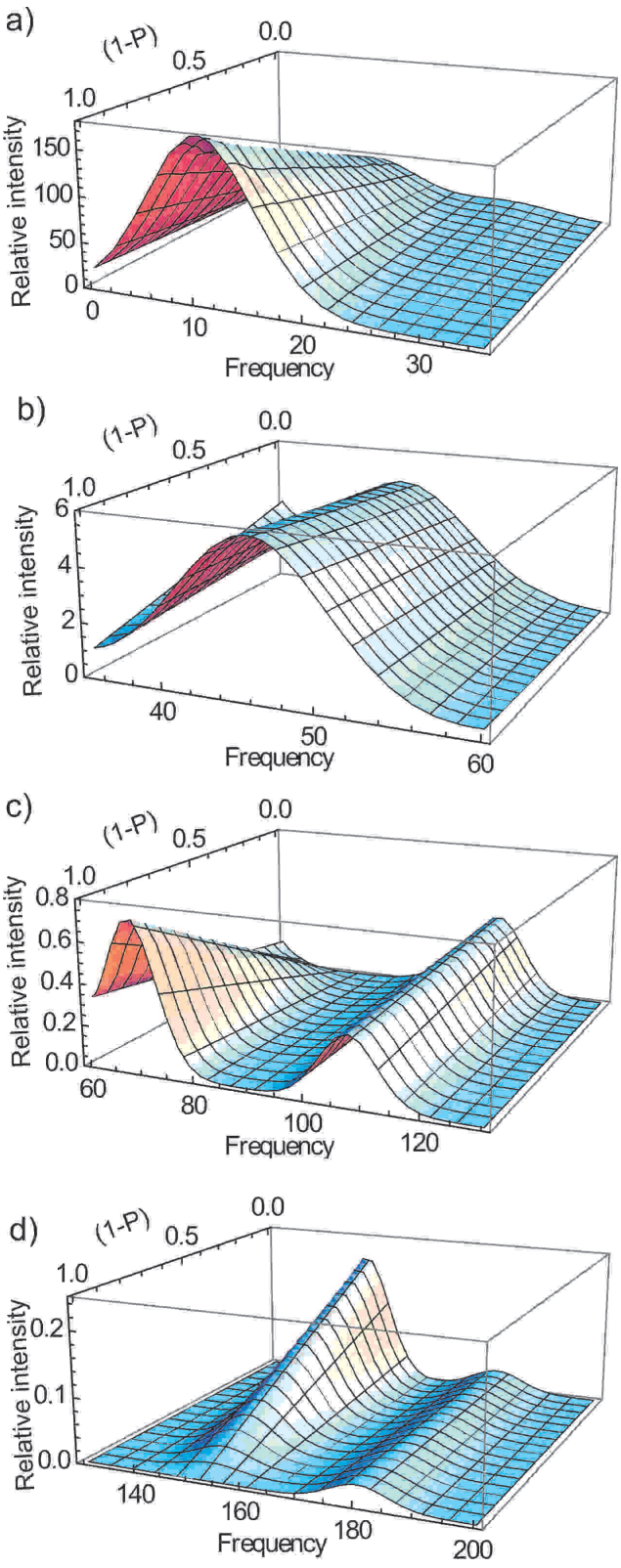

Figure 3: The low-frequency Raman spectra of Z-DNA with different filling of the ion-phosphate lattice by Mg^{2+} counterions. a) Backbone vibration range (0÷40) cm^{-1}(**B**). b) Intranucleoside vibrations range (40÷60) cm^{-1} (**S**). c) H-bond stretching vibrations range (60÷130) cm^{-1} (**H**). d) Ion-phosphate vibrations range (130÷200) cm^{-1} (**Ion**).

of DNA in Z-form of the double helix are built for different degree of filling (P) of the ion-phosphate lattice by Mg^{2+} counterions (Fig. 3). The parameter P equals to 1 if all dimers of Z-DNA contain Mg^{2+} counterions, and P equals to 0 if there is no counterions in dimers. The mode intensities are normalized per intensity of the mode ω_{H1}. The halfwidth of spectra lines is considered equaled to 5 cm^{-1}

The obtained spectrum is divided into four ranges with similar intensities of the modes of DNA conformational vibrations (Fig. 3a – 3d). The range (0÷40) cm^{-1} (Fig. 3a) is characterized by the modes of backbone vibrations (**B**). This modes are the most intensive in DNA low-frequency spectra because their energy is lower than k_BT at room temperatures. Due to the high intensity the modes of backbone vibrations are observed in the experimental spectra as a peak near 25 cm^{-1} [36]. Increasing the filling of the ion-phosphate lattice by Mg^{2+} counterions in the dimers the intensity of this band decreases.

At frequency range (40÷60) cm^{-1} (Fig. 3b) there is a band characterizing the intranucleoside vibrations (**S**). The intensity of this band is essentially lower than the intensity of **B** band formed by modes of backbone vibrations. Therefore in the experimental spectra [36] **S** band is observed as a weak mode near 45 cm^{-1}. The dependence of intensity of this band on filling parameter P is weak.

The frequency range (60÷130) cm^{-1} (Fig. 3c) is characterized by two bands 70 and 110 cm^{-1} that are caused by the modes of H-bond stretching in the base pairs (**H**). The intensity of the band 70 cm^{-1} decreases as the filling of the ion-phosphate lattice by Mg^{2+} counterions increases, while the intensity of the band 110 cm^{-1} remain the same. The comparison of the calculated spectra (Fig. 3c) with the experimental Raman spectra [23, 36] show that at these frequencies there are two strong modes. The frequency and intensity of the observed modes agree with our calculations.

At the spectra range (130÷200) cm^{-1} (Fig. 3d) there are two bands 150 and 180 cm^{-1} characterizing the ion-phosphate vibrations of Mg^{2+} and Na^{+} counterions, respectively (**Ion**). The dependence of intensity on filling parameter P is essential only in case of the mode of ion-phosphate vibrations of Mg^{2+} counterions. The comparison with the experimental spectra show that in the Raman spectra of Z-DNA very weak mode near 153 cm^{-1} is observed [36] that corresponds to the calculated band 150 cm^{-1}. The vibrations of Na^{+} counterions are not observed in the low-frequency spectra of Z-DNA. However, in the spectra of dry DNA films the mode resembling the mode of ion-phosphate vibrations has been detected [22, 25, 30, 31].

4 Conclusions

The conformational vibrations of Z-DNA are studied considering the double helixes with counterions as the lattice of ionic type (ion-phosphate lattice). To find vibrational modes of the ion-phosphate lattice the phenomenological model is developed taking into consideration the feature of Z-DNA structure. In the model the monovalent counterions are localized outside of the double helix, and bivalent counterions are localized between phosphate groups of nucleotide dimers of Z-DNA. Using the developed model the frequencies and the Raman intensities of vibrational modes are calculated for DNA with Na^{+} and Mg^{2+} counterions. The results show that the obtained frequencies of H-bond stretching in nucleotide pairs and the frequencies of intranucleoside vibrations differ from respective frequencies in case of the right-handed DNA double helix. The reason of such difference is in the dimeric structure of the left-handed Z-DNA. New mode of ion-phosphate vibrations about the frequency 150 cm^{-1} is determined, which charac-

terizes the vibrations of Mg^{2+} counterions. The intensity of this mode is rather large, and it is observed in the experimental Raman spectra of Z-DNA [36]. The modes of ion-phosphate vibrations in case of Na^+ counterions (180 cm^{-1}) are weak and do not observed experimentally. The modes of Z-DNA conformational vibrations are very sensitive to the concentration of Mg^{2+} counterions in the solution. The developed model describes the conformational vibrations of Z-DNA with Na^+ and Mg^{2+} counterions and allows determine the origin of new modes in the experimental low-frequency Raman spectra of Z-DNA.

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Appendix: Equations of motion

For a more convenient form of the equations of motion the following variables are used: $Y_c^n = Y_{11}^n + Y_{22}^n$, $y_c^n = Y_{11}^n - Y_{22}^n$, $\theta_c^n = \theta_{11}^n + \theta_{22}^n$, $\eta_c^n = \theta_{11}^n - \theta_{22}^n$, $\rho_c^n = \rho_{11}^n + \rho_{22}^n$, $r_c^n = \rho_{11}^n - \rho_{22}^n$, $Y_g^n = Y_{21}^n + Y_{12}^n$, $y_g^n = Y_{21}^n - Y_{12}^n$, $\theta_g^n = \theta_{21}^n + \theta_{12}^n$, $\eta_g^n = \theta_{21}^n - \theta_{12}^n$, $\rho_g^n = \rho_{21}^n + \rho_{12}^n$, $r_g^n = \rho_{21}^n - \rho_{12}^n$, $\xi_1^n = \xi_{21}^n + \xi_{12}^n$, $\xi_2^n = \xi_{21}^n - \xi_{12}^n$. As the result the equations of motion (8) for the optic long wave vibrations are split into two subsystems of coupled equations:

$$
\begin{cases}
\ddot{Y}_c^n + \frac{m_c b_c}{M_c}\ddot{\rho}_c^n + \frac{m_c l_c^s}{M_c}\ddot{\theta}_c^n + \frac{M_a}{M_c}\gamma_{a0} Y_c^n - g_{yc}(Y_c^n - Y_g^n) + \\
\alpha_c\left(Y_g^n + Y_c^n + l_c^s\theta_g^n + l_c^s\theta_c^n + b_g\rho_g^n + b_c\rho_c^n\right) = 0\,; \\
\ddot{Y}_g^n + \frac{m_g b_g}{M_g}\ddot{\rho}_g^n + \frac{m_g l_g^s}{M_g}\ddot{\theta}_g^n + \frac{m_a}{M_g}(\ddot{Y}_g^n + \ddot{\xi}_1^n) - g_{yg}(Y_c^n - Y_g^n) + \\
\alpha_g\left(Y_g^n + Y_c^n + l_g^s\theta_g^n + l_c^s\theta_c^n + b_g\rho_g^n + b_c\rho_c^n\right) = 0\,; \\
\ddot{\theta}_g^n + \ddot{Y}_g^n\frac{a_g}{l_g} + \beta_g\theta_g^n - g_{\theta g}(\theta_c^n - \theta_g^n) + \alpha_g\frac{M_g a_g}{m_g l_g}\left(Y_g^n + Y_c^n + l_c^s\theta_g^n + l_c^s\theta_c^n + b_g\rho_g^n + b_c\rho_c^n\right) = 0\,; \\
\ddot{\theta}_c^n + \ddot{Y}_c^n\frac{a_c}{l_c} + \beta_c\theta_c^n - g_{\theta c}(\theta_c^n - \theta_g^n) + \alpha_c\frac{M_c a_c}{m_c l_c}\left(Y_g^n + Y_c^n + l_g^s\theta_g^n + l_c^s\theta_c^n + b_g\rho_g^n + b_c\rho_c^n\right) = 0\,; \\
\ddot{\rho}_g^n + b_g\ddot{Y}_g^n + \sigma_g\rho_g^n - g_{\varrho g}\left(\rho_c^n - \rho_g^n\right) + \alpha_g\frac{M_g b_g}{m_g}\left(Y_g^n + Y_c^n + l_g^s\theta_g^n + l_c^s\theta_c^n + b_g\rho_g^n + b_c\rho_c^n\right) = 0\,; \\
\ddot{\rho}_c^n + b_c\ddot{Y}_c^n + \sigma_c\rho_c^n - g_{\rho c}(\rho_c^n - \rho_g^n) + \alpha_c\frac{M_c b_c}{m_c}\left(Y_g^n + Y_c^n + l_g^s\theta_g^n + l_c^s\theta_c^n + b_g\rho_g^n + b_c\rho_c^n\right) = 0\,; \\
\ddot{Y}_g^n + \ddot{\xi}_1^n + \gamma_0\xi_1^n = 0\,;
\end{cases}
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$$
\begin{cases}
\ddot{y}_c^n + \frac{m_c b_c}{M_c}\dddot{r}_c^n + \frac{m_c l_c^s}{M_c}\ddot{\eta}_c^n - \frac{M_a}{M_c}\gamma_{a0}\left(2y_a^n - y_c^n\right) + g_{yc}\left(y_c^n + y_g^n\right) + \\
\alpha_c\left(y_g^n + y_c^n + l_g^s\eta_g^n + l_c^s\eta_c^n + b_g r_g^n + b_c r_c^n\right) = 0\,; \\
\ddot{y}_g^n + \frac{m_g b_g}{M_g}\dddot{r}_g^n + \frac{m_g l_g^s}{M_g}\ddot{\eta}_g^n + \frac{m_a}{M_g}(y_g^n + \xi_2^n) + g_{yg}(y_c^n + y_g^n) + \\
\alpha_g\left(y_g^n + y_c^n + l_g^s\eta_g^n + l_c^s\eta_c^n + b_g r_g^n + b_c r_c^n\right) = 0\,; \\
\ddot{\eta}_g^n + \ddot{y}_g^n\frac{a_g}{l_g} + \beta_g\eta_g^n + g_{\theta g}\left(\eta_c^n + \eta_g^n\right) + \alpha_g\frac{M_g a_g}{m_g l_g}\left(y_g^n + y_c^n + l_g^s\eta_g^n + l_c^s\eta_c^n + b_g r_g^n + b_c r_c^n\right) = 0\,; \\
\ddot{\eta}_c^n + \ddot{y}_c^n\frac{a_c}{l_c} + \beta_c\eta_c^n + g_{\theta c}\left(\eta_c^n + \eta_g^n\right) + \alpha_c\frac{M_c a_c}{m_c l_c}\left(y_g^n + y_c^n + l_g^s\eta_g^n + l_c^s\eta_c^n + b_g r_g^n + b_c r_c^n\right) = 0\,; \\
\ddot{r}_g^n + b_g\ddot{y}_g^n + \sigma_g r_g^n + g_{\varrho g}\left(r_c^n + r_g^n\right) + \alpha_g\frac{M_g b_g}{m_g}\left(y_g^n + y_c^n + l_g^s\eta_g^n + l_c^s\eta_c^n + b_g r_g^n + b_c r_c^n\right) = 0\,; \\
\ddot{r}_c^n + b_c\ddot{y}_c^n + \sigma_c r_c^n + g_{\rho c}\left(r_c^n + r_g^n\right) + \alpha_c\frac{M_c b_c}{m_c}\left(y_g^n + y_c^n + l_g^s\eta_g^n + l_c^s\eta_c^n + b_g r_g^n + b_c r_c^n\right) = 0\,; \\
\ddot{y}_g^n + \ddot{\xi}_2^n + \gamma_0\xi_2^n = 0\,; \\
2\ddot{y}_a^n + 2\gamma_{a0}\left(2Y_a^n - y_c^n\right) = 0\,,
\end{cases}
$$

where $\alpha_g = \alpha/M_g$, $\alpha_c = \alpha/M_c$, $\beta_g = \beta/m_g l_g^2$, $\beta_c = \beta/m_c l_c^2$, $\sigma_g = \sigma/m_g$, $\sigma_c = \sigma/m_c$, $\gamma_0 = \gamma/m_a$, $\gamma_{a0} = \gamma_a/M_a$, $g_{\theta g} = g_\theta/m_g l_g^2$, $g_{\theta c} = g_\theta/m_c l_c^2$, $g_{\rho g} = g_\rho/m_g$, $g_{\rho c} = g_\rho/m_c$, $g_{yg} = g_y/m_g$, $g_{yc} = g_y/m_c$, $a_c = \sin\theta_{0c}$, $a_g = \sin\theta_{0g}$, $b_c = \cos\theta_{0c}$, $b_g = \cos\theta_{0g}$, $l_c^s = l_c\sin\theta_{0c}$, $l_g^s = l_g\sin\theta_{0g}$.

The first subsystem of equations of motion describes symmetric vibrations of nucleotides in the dimers, while the second subsystem describes antisymmetric vibrations of nucleotides. The obtained equations of motions are solved using the substitution: $q_n = \tilde{q}_n \exp(i\omega t)$, where $\tilde{q}_n$ and ω are amplitude and frequency for some coordinate of vibrations, respectively. As the result the equation for frequencies of long-wave vibrations of Z-DNA are obtained. From the first subsystem of equations of motion the equation for frequencies ω_{H1}, ω_{H3}, ω_{S2}, ω_{S3}, ω_{B2}, ω_{B4}, and ω_{Ion1} is derived. The second subsystem of equations of motion gives the equation for frequencies ω_{H2}, ω_{H4}, ω_{S1}, ω_{B1}, ω_{B3}, ω_{Ion2}, and ω_{Ion3}. Using the parameters discussed in the section 2 the frequency values of the modes of Z-DNA conformational vibrations are calculated numerically. The values of the calculated frequencies are showed in the Table 1.

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